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LACTOPRENE EV is an acrylic copolymer made from a monomer charge composed of 95 percent ethyl acrylate and 5 percent chloroethyl vinyl ether. The copolymer itself contains about 97 percent ethyl acrylate and slightly more than 3 percent chloroethyl vinyl ether. The properties of this material and other acrylic elastomers, and their preparation on a laboratory scale, have been described in several papers (1-17).

Lactoprene EV in the pilot plant, along with other polymers and copolymers of acrylic esters, has been produced at the Eastern Regional Research Laboratories on a rather small scale, i.e., in a glass-lined batch polymerizer of 10-gallons capacity. Recently it has been made in 80-gallon reactors at the Government Laboratories operated by the University of Akron as agent for the Office of Synthetic Rubber.

In this work, an emulsion polymerization system was employed because it is generally used and understood by

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industry. It is relatively easy to control and gives a product in latex form for which there are many uses. With further processing, this system also gives a solid elastomer for which there is a wide field of application. In general, the process may also be used in making other acrylic polymers and copolymers.

Because of the interest shown by industry in the special properties of Lactoprene EV, it was thought desirable to describe at this time some of the pilot-plant work on the elastomers.

Process

In producing Lactoprene EV, the ethyl acrylate monomer, a liquid at room temperature, is first washed with caustic soda to remove the inhibitor (Figure 1). The washed monomer is premixed with the chloroethyl vinyl ether comonomer, also a liquid, which is normally stored without inhibitor. After water, emulsifiers, and part of the catalyst solution have been added to the charge tank and mixed, the premixed monomers are added. This mixture is then charged to the polymerizer,
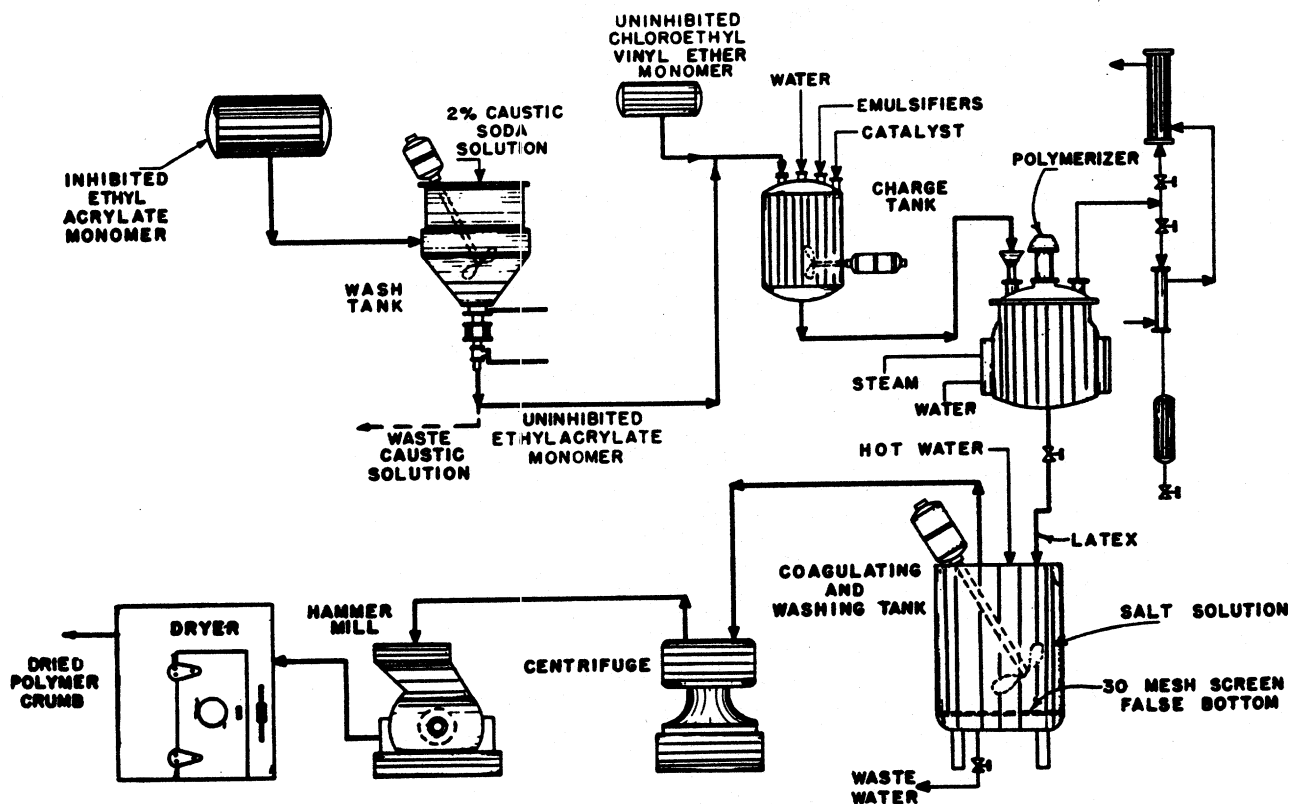

FIG. 1--Flow sheet of the Lactoprene EV process.

FIG. 2—10-Gallon polymerization unit.

monomer is vigorously shaken with about an equal volume of 2 percent caustic solution. The appearance of any color in the caustic solution layer in less than 1 minute indicates the need for additional washing.

As chloroethyl vinyl ether is not so active as the ethyl acrylate, it is usually uninhibited and is ready for use as received.

Polymerization: The emulsion polymerization of the acrylates was carried out under atmospheric reflux conditions. As the acrylates polymerize at an extremely high rate initially, another method for dissipating the heat of reaction, in addition to the normal one through the jacket of the reactor, was considered desirable. The reflux condenser serves this purpose, as it removes the heat of polymerization primarily by refluxing volatile materials in the charge. This method of heat removal is quick and positive.

Another advantage of this type of polymerization is that its progress can be observed by noting the refluxing temperature of the charge, i.e., as the conversion progresses, the temperature of the charge increases.
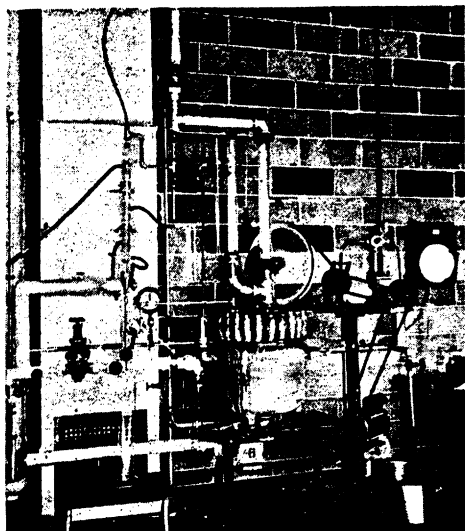
which is equipped with a reflux condenser, and operated at atmospheric pressure.

The charge is heated by steam (and later hot water) to the refluxing temperature. After a few minutes at the initial refluxing temperature of 82° C., the polymerization starts vigorously. Part of the heat generated by the polymerization is removed in the reflux condenser and part by the cooling jacket. The reaction continues fairly vigorously until a temperature of about 86° C. is reached, when more catalyst solution is added to maintain the polymerization at a reasonable rate. Heat is also applied through the jacket as required.

When the temperature of the charge reaches 95 to 96° C., the rate of polymerization is slow and the conversion is about 95 percent complete. The unreacted monomers are then stripped with live steam. The total cycle from charging the polymerizer to cooling the latex requires about 3 hours.

If the elastomer is to be obtained in solid form, the latex product is slowly drained from the polymerization kettle into a hot, agitated salt solution, which coagulates it in the form of small granular pieces resembling cottage cheese. The coagulated rubber crumb is washed with hot water to remove the salt and emulsifiers.

The washed elastomer particles can be dewatered in a centrifuge. In most cases this forms a mat, which must be passed through a hammer mill to disintegrate it for drying in a through-circulation air dryer. The elastomer crumb is dried at about 200° F. for approximately one hour. It is then ready for fabrication.

Operations

Purification of Monomer: The ethyl acrylate monomer as received is usually inhibited with about ¼ of 1 percent hydroquinone, which must be removed. This may be done by washing the monomer about three times with 2 percent caustic soda solution, the volume of each wash being equal to approximately one-third of the volume of the monomer. The washing can best be accomplished in a cone-bottom wash tank equipped with a bottom sight glass. Agitation time for each wash should be about 5 minutes before the waste caustic solution is allowed to settle and drain off.

With careful manipulation, monomer losses can be held between 5 and 10 percent. To determine whether additional washing is required, a small amount of the

A = REFLUX CONDENSER
B = SIGHT GLASS
C = CATALYST SOLUTION
D = CHARGING LINE. FUNNEL REPLACED BY RUPTURE DISC DURING OPERATION
E = 10 GALLON POLYMERIZER
F = RECORDING THERMOMETER
G = STRIPPING TAKE-OFF
H = COOLER
I = WATER TO POLYMERIZER JACKET
J = STEAM TO POLYMERIZER JACKET
K = STEAM CONDENSATE RETURN
L = STEAM FOR STRIPPING
M = WATER FOR FLOODING CHARGE
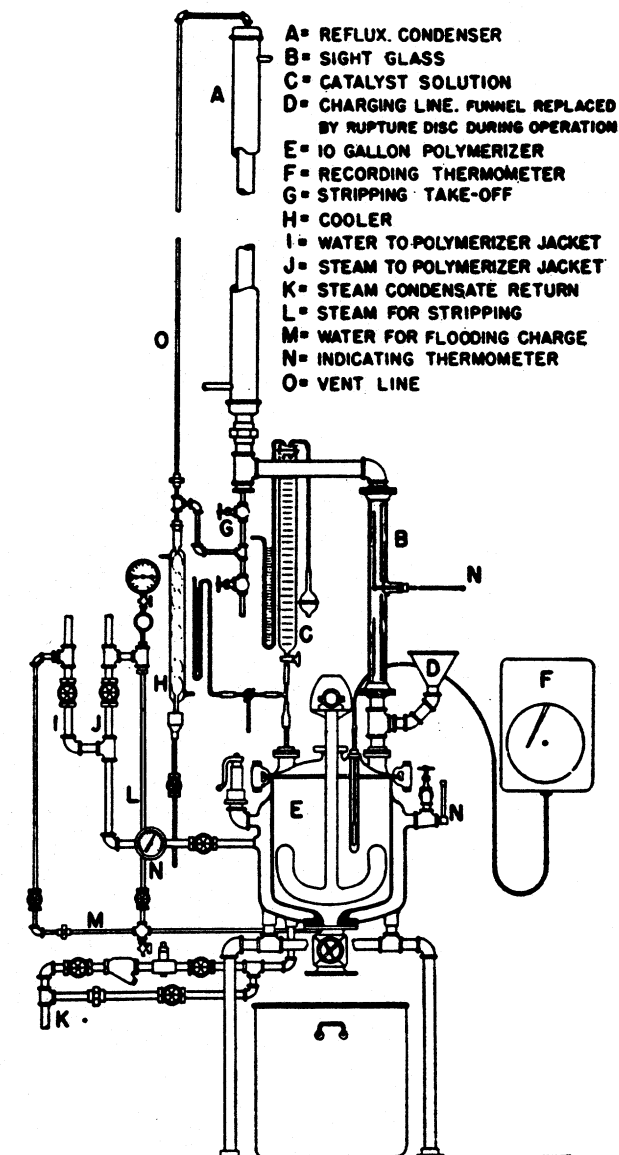N = INDICATING THERMOMETER
O = VENT LINE

FIG. 3—Schematic view of the 10-gallon polymerization unit.

As previously mentioned, the polymerization unit (Figures 2 and 3) is of 10-gallon capacity and has a heating jacket with slightly more than 5 square feet of surface area. It is glass-lined and equipped with an anchor-type agitator driven between 10 and 80 r.p.m. by a variable speed drive. A 2-inch diameter glass sight section between the reflux condenser and the kettle enables the operator to observe the refluxing and also any foaming tendencies of the charge. The reflux condenser, 2 inches in diameter by 5.5 feet long, contains about 3 square feet of condensing surface. A take-off line at the bottom of the reflux condenser leading to a cooler is used in the stripping operation.

Automatic controls have not been used. No difficulties were encountered in controlling by hand, particularly after the diameter of the reflux condenser was enlarged from 1 to 2 inches to prevent vapor-liquid binding, and the condensing surface was increased from 1½ to 3 square feet. However, as a precaution in case the reaction becomes uncontrollable, the charge can be flooded with water from a line provided for this purpose.

Several emulsifying systems for polymerizing the monomers have been studied in the pilot plant. Probably one of the best for general use is the one in which 1.2 percent (moisture-free basis) Tergitol Penetrant No. 4 and 0.8 percent (moisture-free basis) Triton 720, based on the total monomers, are used.* Latex made by this system is easy to coagulate; it is merely necessary to add the latex slowly to a hot, agitated brine solution to obtain the elastomer in small granular particles. Although some other emulsifying systems are more stable in the polymerizer, when the foregoing emulsifiers and a charge containing about 40 percent monomers are used, as many as four runs can be made in the 10-gallon unit before cleaning is necessary.

Table I shows a typical charge formula for this low-solids Lactoprene EV latex. The water, a part of the catalyst solution, and the emulsifiers are added to the charge tank, and agitated to assist solution of the emulsifiers. The two monomers are then premixed and added, and the total charge is then added to the polymerization unit. Only a small amount of catalyst is required because of the reflux polymerization method. About 0.005 percent of ammonium persulfate is required, based on the monomers. To decrease the intensity of the polymerization at the start, only a part of the catalyst, say about 40 or 50 percent, is added to the charge; more catalyst is added later as the polymerization rate decreases. The agitation rate for most of the runs has been about 38 r.p.m.

After charging, steam is applied to the jacket until the temperature of the charge reaches about 75° C., at which point the heating system is changed to hot water at about 99° C. by using the steam-water mixer. Refluxing starts

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* Mention of products or companies should not be construed as a recommendation or endorsement by the Department of Agriculture or the Office of Synthetic Rubber over others not mentioned.
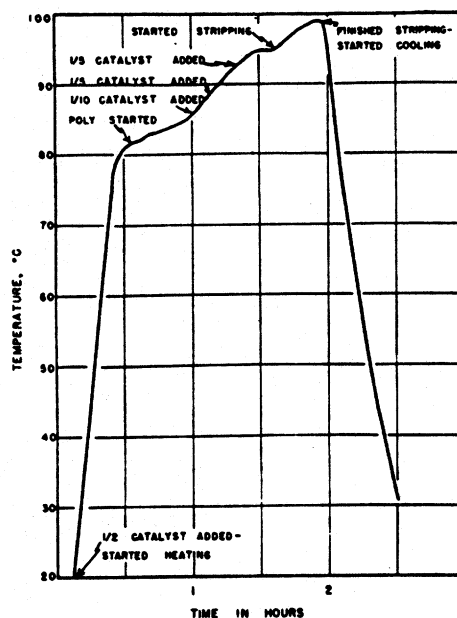

FIG. 4 — Polymerization temperature curve (40% monomer concentration).

at 82° C., and after a few minutes vigorous polymerization begins (Figure 4). Refluxing may be indicated first by a slight fluctuation in the manometer attached to the polymerizer, thus making it possible to apply cooling water to the jacket before the reaction becomes too vigorous.

As mentioned before, most of the heat of polymerization is dissipated through a reflux condenser. The heat generated vaporizes monomer and water, which in turn are condensed in the reflux condenser and return hot to the system. No difficulty is encountered in re-emulsifying the returned monomer, and apparently refluxing of the monomer has little effect upon the particle size of the finished latex, most of the particles being less than 0.5 μ in diameter. With an adequate reflux condenser capable of removing the heat of polymerization, the tendency has been to use the jacket of the 10-gallon unit primarily for heating purposes, i.e., for raising the temperature of the charge to its starting reflux point and for the later part of the polymerization.

As the polymerization proceeds, the reaction begins to slow down at about 85 to 86° C., and it is necessary to add the remainder of the catalyst solution, approximately in one-tenth increments. It is also necessary to apply heat to the jacket from this point until the end of the run. By the end of the last catalyst addition, the temperature is about 95 or 96° C., and about 95 percent of the monomers have been polymerized. Figure 5 shows a typical conversion curve for Lactoprene EV.

At this point, the rate of reaction is extremely low. The unreacted monomers are then stripped with live steam injected into the bottom of the charge. The jacket temperature is held at 100° C. with hot water. About one-half hour is required to strip these monomers. Because of the foaming tendency of the latex, the stripping operation has to be carried out rather slowly. The percentage of stripped monomers that can be subsequently polymerized has not been determined.

For preparing a latex that is more stable and has a higher solids content about 55 percent, a good emulsifier system consists of 3 percent (moisture-free basis) Triton 720 and 1 percent Triton R-100, based on the total

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TABLE I—CHARGE FORMULA A FOR LOW-SOLIDS LACTOPRENE EV LATEX

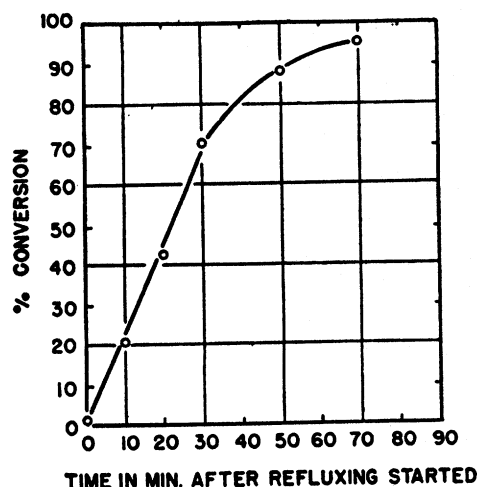| Ingredients	Pounds	Parts by weight
Ethyl acrylate	20.0	95.0
Chloroethyl vinyl ether	1.05	5.0
Water	31.7	151.0
Tergitol Penetrant No. 4 Paste (m.f.b.)	0.25	1.2
Triton 720 (m.f.b.)	0.16	0.8
Ammonium persulfate	0.0011	0.0052

FIG. 5—*Polymerization conversion curve.*

monomers. The Triton R-100, a dispersing agent, has been added primarily for the purpose of decreasing the viscosity peak of the charge in order to permit uniform and rapid dissipation of the heat of polymerization to the cooling mediums.

Table II shows a typical charge formula for this high-solids Lactoprene EV latex, which is more stable to coagulation. Figure 6 shows a temperature curve for this type of run.

Coagulating and Washing: The equipment used for coagulating and washing the elastomer consists of a 25-gallon stainless steel tank equipped with an agitator, baffle and false bottom.

In coagulating, the hot 40 percent latex is slowly drained from the polymerizer into the stainless steel tank containing an agitated brine solution composed of 10 pounds of salt (NaCl) in 10 gallons of water at 180° F. The latex coagulates into small, granular, porous pieces, which are easily washed. Washing the elastomer with hot water to free it of salt may be done batchwise or continuously in the same tank; the hot water is added at the top, and waste water is withdrawn through a false bottom. As the coagulum is similar in physical form to GR-S crumb, it is probable that a continuous rotary vacuum filter such as that used in some of the GR-S plants could be used in washing and dewatering the Lactoprene crumb. Because of lack of proper equipment, this procedure has not yet been tried at this laboratory.

The more stable 55 percent latex is not satisfactorily coagulated with salt; therefore, a method has been developed in which an aluminum sulfate solution is used. In this procedure, 15 parts of 3 percent $Al_2(SO_4)$ $3.18H_2O$ solution are slowly added to 100 parts of the agitated cooled latex, causing it to thicken or cream. The

creamed latex is then added to about 1000 parts of agitated water at a temperature of approximately 130 to 140° F. The elastomer coagulates in the form of small particles, which are easily washed by the procedure described above. The particle size may be varied by varying the temperature of the coagulating water used in the process.

Dewatering and Drying: The washed elastomer from either of these two methods, suspended in water, is passed over a vibrating screen to remove free draining water and then is loaded on drying trays. An alternative method is to dewater the elastomer in a centrifuge. This, however, may cause the rubber to form a mat, which requires hammer milling to disintegrate it. The elastomer is then loaded on trays and dried in a through-circulation air dryer for approximately one hour at a temperature of about 200° F. As the elastomer is resistant to degradation by oxidation and sunlight, it may be stored indefinitely.

Polymerizations in 80-Gallon Reactors

To conduct polymerizations on a pilot-plant scale larger than the 10-gallon unit, arrangements were made with the Office of Synthetic Rubber to carry out the Lactoprene EV polymerization in equipment available at the Government Laboratories in Akron, operated by the University of Akron. After a few preliminary runs in 5-gallon reactors to test the efficacy of the raw materials and to determine the most suitable charging procedure, the desired polymerizations were made in glass-lined 80-gallon reactors.

Figure 7 shows a diagram of an 80-gallon reactor with its reflux and control system. The system was designed to operate at 125 pounds per square inch gage, but may be operated at pressures as low as 200 millimeters of mercury, absolute (the minimum pressure attainable with the vacuum jets). For these runs, a relief valve, set to open at 3 pounds per square inch, was installed in the vent line at the top of the noncondensable vapor trap.; the main purpose of the relief valve was to provide a means of controlling the venting of noncondensable vapors from the system.
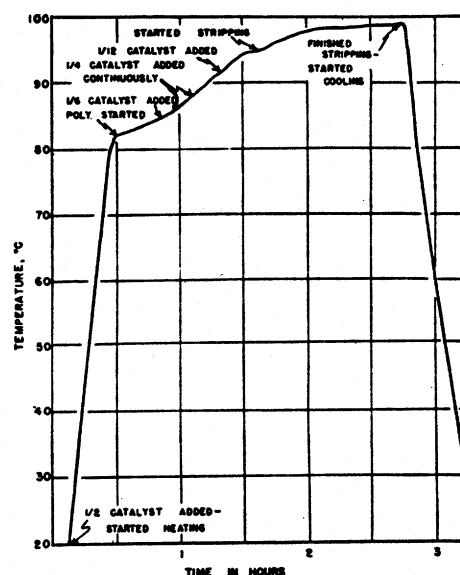
TABLE II—CHARGE FORMULA B FOR HIGH-SOLIDS LACTOPRENE EV LATEX

Ingredients	Pounds	Parts by weight
Ethyl acrylate	23.1	95.0
Chloroethyl vinyl ether	1.2	5.0
Water	19.9	82.0
Triton 720 (m.f.b.)	0.72	3.0
Triton R-100	0.24	1.0
Ammonium persulfate	0.0013	0.0053

FIG. 6 — *Polymerization temperature curve (55% monomer concentration).*

Operations in 80-Gallon Reactors

Successful runs were made in accordance with the two charge formulas used in the 10-gallon reactors, except that potassium persulfate was used as the catalyst instead of ammonium persulfate. Table III shows the charge formulas.

The inhibitor was removed from the ethyl acrylate by the method used for charges in the 10-gallon reactor, except that the time for each step was somewhat longer because of the greater quantity of material handled.

For Formula A, charge factors of 1.2, 2.12, and 2.4 pounds per part were used, which represented loadings of 45, 80, and 90 percent, respectively. For Formula B, charge factors of 1.79, 2.15, and 2.51, which represented loadings of 50, 60, and 70 percent, respectively, were used. The water, containing the dissolved emulsifiers, was charged to the reactor first. Five pounds of water were withheld for solution of the catalyst portions, and 25 pounds were reserved for rinsing the charging equipment and lines.

Agitation was started, and the premixed monomers were charged. Because of the instability of potassium persulfate during prolonged heating above 140° F., the catalyst was withheld until the internal temperature of the reactor reached 180° F. The catalyst was added in increments as required to sustain the polymerization. However, if careful control was maintained, the total amount of catalyst required could be added initially.

The temperature of polymerization was controlled by circulating water through the jacket of the reactor and by refluxing the boiling monomers. The temperature of the batch during refluxing was between 180° and 210° F., provided the pressure in the system was below 3 pounds per square inch. In several cases, when the reaction rate was too high and difficult to control, the
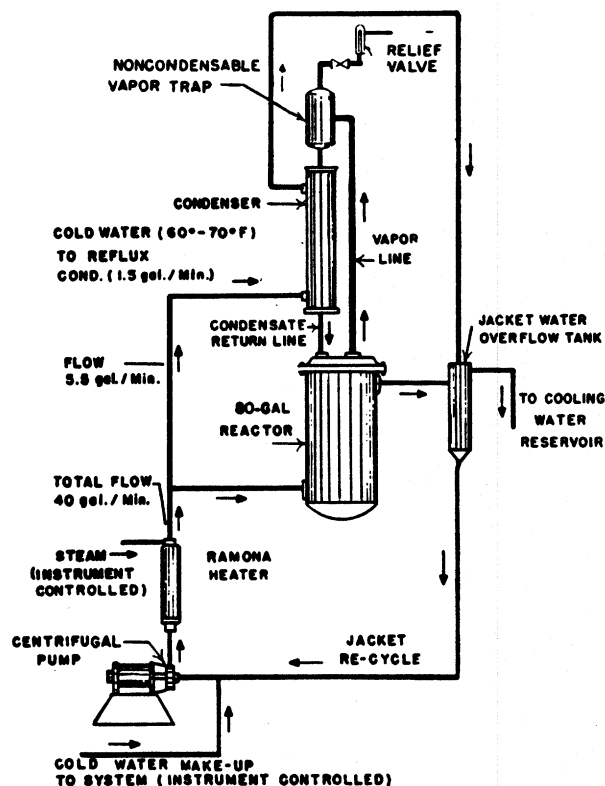
valve in the line between the noncondensable vapor trap and the relief valve was closed, allowing the temperature and pressure to rise; maximum temperatures and pressures of 260° F. and 60 pounds per square inch were attained.

The heating and cooling system was designed and operated so that a definite temperature differential was maintained between the temperature of the water in the jacket of the reactor and that in the jacket of the condenser. The temperature differential was adjusted so that the temperature in the jacket of the condenser was low enough to condense the monomer vapors but not low enough for the pressure drop between the reactor and the condenser to cause excessive foaming and allow a large quantity of latex to surge into the condenser.

The discharge valve of the pump for circulating water through the jackets was set to deliver 40 gallons per minute. The water from the pump plus the added water from heating steam was split into two streams; 5.5 gallons per minute were diverted to the jacket of the condenser, and the remainder was delivered to the reactor jacket. One and one-half gallons per minute of cold water, at a temperature of 60 to 70° F., were added to the stream going to the jacket of the reflux condenser. With these flow rates and a condensing surface area of 38 square feet, a temperature differential of 25° to 35° F. was attained when the internal temperature of the batch was 180° F. before the reaction was initiated and up to 210° F. after most of the polymerization had occurred.

Stripping was accomplished at a temperature of 140° to 160° F. and a vacuum of 20 to 24 inches of mercury. Internal steam was used in stripping the latex prepared by Formula A, but none was used in stripping the high-solids latex. With both types of latex, it was necessary to reduce the vacuum during the preliminary stages of stripping to prevent excessive foaming.

The Lactoprene EV prepared in accordance with Formula A was coagulated by adding 1 part of latex at 180° F. to 2 parts of an agitated 10 percent sodium chloride solution at 150° F. The latex prepared according to Formula B was creamed with 15 parts of a 3 percent solution of alum per 100 parts of latex. The creamed latex was coagulated by pumping 1 part into 10 parts of agitated water at 130° to 140° F. The crumb from both types of coagulation was washed free of salt with hot water and subsequently dried at 200° F. The regular GR-S salt-acid method of coagulation was unsuccessful with small samples of both types of latex.

Fifty gallons of low-solids latex from Batches 14HGA1, 14HGA2, and 14HGA3 (Table IV) were coagulated to produce XP-102-L2 polymer. The remaining latex of these batches, blended with Batch 14HGA4, was coagulated for XP-101-L1 polymer. Batch 14HGB5

FIG. 7—80-Gallon polymerization unit with reflux system.

TABLE IV—POLYMERIZATION DATA

Charge formulas	Polymerization batch no.	Product no.	Conv. (%)	Total solids (%)	React. time* (Hrs.)	Mooney viscosity (ML-4)	Poly. temp.† (°F.)
A	14HGA1, 14HGA2, 14HGA3, 14HGA4	XP-101-L1 and XP-101-L2 (polymer)	85	34	1.8	54	190-200
B	14HGB5	XP-102-L1 (high-solids latex)	93	52	1.5	58	190-200
B	14HGB4	XP-103-L1 (polymer)	90	50	0.8	44	180-260
B	14HGB1, 14HGB2	XP-103-L2 (polymer)	—	—	3.0	58	195-210

* Time for 90 percent of the total conversion. Induction period, when an insufficient amount of catalyst was charged initially, is not included. † Temperature at which 90 percent of the conversion occurred.

of high-solids latex was used for XP-102-L1 (latex), 14HGB1 and 14HGB2 were coagulated for XP-103-L2 (polymer) and 14HGB4 for XP-103-L1 (polymer).

Chemical tests and screening tests for physical properties were made on these polymers.

Polymerization: Table IV shows polymerization data for the two types of latex. The amount of potassium persulfate needed to initiate the reaction of Batches 14HGA1 through 14HGA4 (used for XP-101-L1 and XP-101-L2) was determined to be 0.00522 part per 100 parts of monomer charged. Batch 14HGA2, however, failed to react with this amount charged initially, possibly because of a trace of inhibitor that remained in the ethyl acrylate.

When the reactor was loaded to 90 and 80 percent of its capacity for Batches 14HGA3 and 14HGA4, respectively, the reflux condenser was flooded after the polymerization was initiated. At a loading of 45 percent for Batches 14HGA1 and 14HGA2, flooding did not occur.

One one-hundreth part of potassium persulfate was determined as the amount necessary to initiate the reaction of the high-solids batches used for XP-102-L1, XP-103-L1, and XP-103-L2. For no accountable reason, the first two batches did not react with this amount, and additional increments of the catalyst were required to initiate the reactions.

Temperatures of Batches 14HGB3 and 14HGB4, in which an excess of catalyst was charged initially, rose from 180° to 250° and 260° F., respectively, in 2 to 3 minutes. As soon as the pressure increased above 3 pounds per square inch and the noncondensable gases were vented, the valve between the noncondensable gas trap and the relief valve was closed, and the pressure in the reactor reached a maximum of 50 and 60 pounds per square inch for Batches 14HGB3 and 14HGB4, respectively. Data are not shown for Batch 14HGB3 because the reaction was stopped at a low conversion by cold water that leaked through a tube sheet of the condenser; the resulting material was discarded.

The reactions in Batches 14HGB3, 14HGB4 and 14HGB5, in which 0.020, 0.0175, and 0.010 part of potassium persulfate, respectively, was charged initially, started rapidly, and about 90 percent of the final conversion for 14HGB4 and 14HGB5 was attained in 0.8 and

1.5 hours, respectively. For these batches, the reactor was charged to 60 percent of its capacity, which was about maximum load for the 80-gallon reactor system.

During polymerization of the high-solids batches, 14HGB3 and 14HGB4, the materials in the reactor flooded the reflux condenser for 15 to 20 minutes. In Batch 14HGB4, the temperature differential between the water in the reflux condenser and that in the reactor jacket ranged from a maximum of 54° to 0° F. at the end of the flooding period, and the temperature differential between the water entering and leaving the condenser was 10° F. When the flooding ceased, the temperature differential of the water across the condenser decreased slowly until the control system required the addition of steam to the circulating water to maintain the temperature of the batch in the reactor above the boiling point of the monomers. The minimum temperature of the cooling water entering the jacket of the reactor was 90° F; that in the jacket of the condenser was slightly lower. In Batch 14HGB5, in which 0.01 part of catalyst was added initially, flooding of the condenser still occurred, but the temperature differentials were smaller, and the maximum internal temperature of the batch was lower than those obtained in previous batches made according to the same formula.

Properties of Raw Polymer

When Lactoprene EV is produced in glass-lined or stainless steel equipment according to methods described for the 10-gallon polymerization unit, the resulting polymer is a white, opaque crumb, which yields water-clear and colorless dispersions in suitable organic solvents. When regular pilot-plant equipment with carbon steel latex transfer lines is used, however, the crumb tends to be yellow or brown. The feed lines to the 80-gallon glass-lined reactors are of stainless steel; the lines between the reactor and stripper are of carbon steel. The lines from the glass-lined stripper are also carbon steel.

Lactoprene EV crude crumb is dry and firm, exhibiting no noticeable tack at room temperature. It can be dispersed in the lower aromatic hydrocarbons, particularly benzene, yielding a water-clear product. The polymerization procedures described in this paper usually do not yield a completely soluble product. It is evident that a sizable gel fraction exists when the polymer is dispersed in acetone instead of benzene. Acetone is a good solvent for Lactoprene EV, but the cloudiness of

TABLE V—CHEMICAL TESTS ON LACTOPRENE EV

Polymer Batch No.	Product No.	Ash (%)	Combined emulsifier (%)	Gel (%)	Swell volume	Dil. solution visc.
14HGA1 14HGA2 14HGA3 14HGA4	XP-101-L1	0.27	0.25	0	—	4.55
14HGA1 14HGA2 14HGA3	XP-101-L2	1.02	0	1.0	—	4.80
14HGB5	XP-102-L2	0.92	0.27-0.35	62	61	2.37
14HGB4	XP-103-L1	0.45	0.375	38	77	2.11
14HGB1 14HGB2	XP-103-L2	0.44	0.30	44	83	2.97

acetone dispersions is indicative of appreciable gel content. The gel is not readily apparent in benzene dispersions because the refractive index of the gel fraction matches that of the benzene.

It is believed that the method of polymerization described in this paper, in which the reaction occurs substantially at reflux temperatures, usually produces side reactions leading to some branching and cross-linking of polymer chains. On the assumption, however, that side reactions occurring at reflux temperatures are likely to introduce excessive disorder in the polymer chains, with a resulting impairment in tensile properties, other methods of polymerization were tried (3). These included solution polymerization and emulsion polymerization at low temperature. None of the polymers so prepared exhibited any significant improvement in tensile properties over those prepared by the method described in this paper. This appeared to be true even though soluble polymers having molecular weights ranging from 300,-000 to 1,000,000 were obtained (3).

Chemical Tests: As expected, because of the small amount of nonvolatile inorganic ingredients charged and the absence of a shortstop and antioxidant, the polymer contained low percentages of ash (0.3 to 1 percent). The low-solids Lactoprene EV contained little or no gel and had high dilute solution viscosity (4.5 to 4.8). The high-solids polymer exhibited a high gel content (40 to 60 percent) and a corresponding reduction in dilute solution viscosity. The gel was determined in accordance with the standard procedure used for GR-S. Table V shows the data for some of the runs in the 80-gallon polymerization unit.

Processibility of Polymer

Lactoprene EV, although essentially a polar polymer, can be handled on standard rubber processing equipment. It requires no initial breakdown on cold rolls. Although the crude product readily bands on warm rolls, the band is not smooth. The material does flow evenly if the mill temperature is sufficiently high. At this temperature, however, the polymer tends to split and go on both rolls. The best processing is obtained at about 160° F.

Some of the polymers prepared in the 80-gallon reactor (the XP series) were compounded with SRF and EPC blacks and compared with standard control stocks prepared from GR-S (X-387). Tables VI and VII give the compounding recipes used and the processing data

TABLE VI—COMPOUNDING RECIPES USED IN COMPARATIVE EVALUATION OF LACTOPRENE EV POLYMERS (XP SERIES) AND GR-S (X-387)

Ingredients	Lactoprene EV A	Lactoprene EV B	GR-S (X-387) C	GR-S (X-387) D
Polymer	100	100	100	100
SRF black [a]	50	—	50	—
EPC black [b]	—	50	—	50
Stearic acid	2	2	—	—
Tetramethyl thiuram monosulfide [c]	1	1	—	—
Triethyltrimethyl triamine [d]	variable [g]	variable [h]	—	—
Sulfur	2	2	2	2
Zinc oxide	—	—	5	5
Coal tar softener [e]	—	—	5	5
Mercaptobenzothiazole [f]	—	—	1.5	1.5

(a) Furnex. (b) Wyex. (c) Monex. (d) Trimene Base. (e) BRT No. 7. (f) Captax. (g) For XP-101-L2 and XP-103-L1, 1 part; for XP-101-L1 and XP-103-L2, 2 parts. (h) For XP-101-L1 and XP-103-L2, 2 parts; for XP-101-L2 and XP-103-L1, 2.5 parts.

TABLE VII—PROCESSING CHARACTERISTICS OF LACTOPRENE EV COMPOUNDS COMPARED WITH THOSE OF GR-S

Product No.	Recipe	Mooney viscosities Raw poly-mer (ML-4)	Mooney viscosities Compounded poly-mer (ML-4)	Mill shrink-age (%)	Rough-ness index	Extrusion index
XP-101-L1	A		71	—	20	9.5
		53				
	B		83	34	17	8.5
XP-101-L2	A		64	42	Too rough	11.5
		54				
	B		77	25	Too rough	11.5
XP-103-L1	A		46	46	148	10.0
		58				
	B		80	27	51	12.5
XP-103-L2	A		71	—	24	9.5
		42				
	B		92	30	17	8.0
GR-S X-387	C	51	50	50	131	9.5
	D	51	68	45	55	11.0

obtained. Comparing Mooney viscosities, mill shrinkage roughness values and extrusion indices, one will observe that Lactoprene EV is processed about as readily as GR-S.

Although similar processing data for Lactoprene EV stocks containing HMF or HAF blacks are not available, judging from experience with these stocks on a 6 by 12-inch laboratory mill and in a Royle No. ½ extruder, one may expect an improvement in the processibility of Lactoprene EV paralleling that in GR-S processing obtainable with these furnace blacks.

Vulcanization

As shown in Table VI, the amount of the basic curative, triethyltrimethyl triamine (Trimene Base), is variable. In certain cases, it is necessary to increase the amount of curative used to compensate for losses, presumably as a result of neutralization by acidic components in the mix; for example, hydrolytic products of the polymerization and acidic compounding ingredients. Considerable care should be given to the amount of amine curative employed in compounding recipes for evaluating the polymer itself.

With sulfur-cured compounds of other rubbers, minor variations in curing characteristics are normally compensated for by varying the curing time at a given temperature, thus establishing the tensile property-curing time relationship for a standard recipe. With acrylic elastomers, it is desirable, at least for preliminary work, to establish curing conditions by varying the amount of amine curative in the recipe. It is necessary to make only one cure (60 minutes at 298° F.) for each variation of the compound.

The concept of optimum cure for evaluation purposes is confused by the practical necessity of using larger amounts of amine (2 to 4 parts per 100 of polymer) to obtain technical cures giving maximum heat resistance. Whenever the molecular structure of the polymer is to be evaluated, it is expedient to cure to a state at which the ultimate tensile strength, that is the tensile strength per square inch, based on the cross-section of the specimen at break, is a maximum. Reversion in modulus and tensile strength occurs with some recipes, but it appears too slowly to be of value in fixing optimum cure. It is, of course, this resistance to reversion which makes this product a heat-resistant rubber.
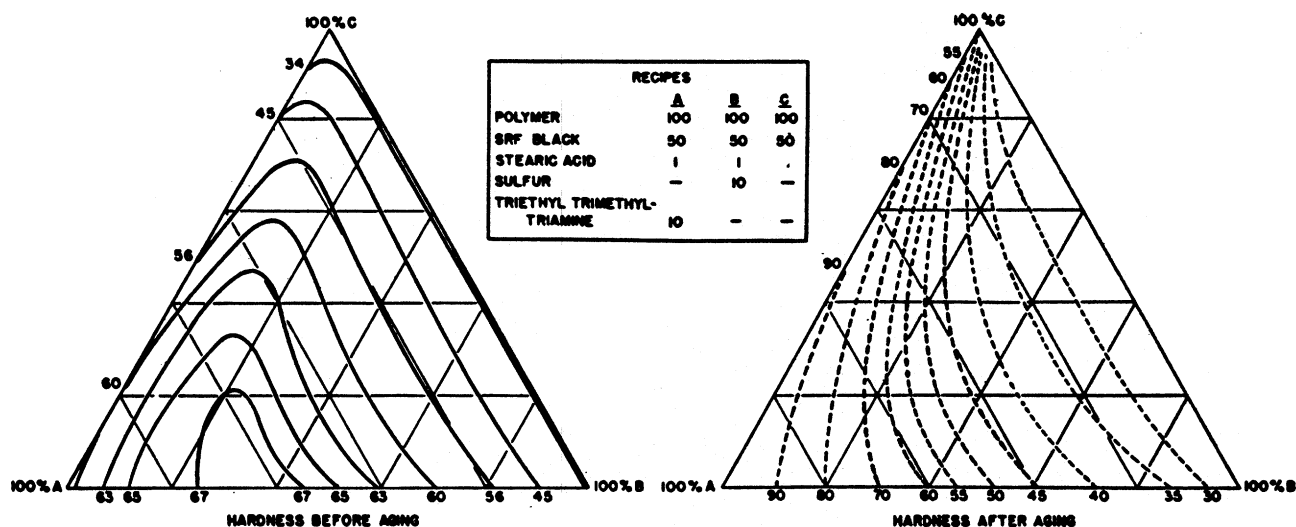
RECIPES			
	A	B	C
POLYMER	100	100	100
SRF BLACK	50	50	50
STEARIC ACID	1	1	.
SULFUR	—	10	—
TRIETHYL TRIMETHYL-TRIAMINE	10	—	—

FIG. 8—*Trilinear compounding chart for Lactoprene EV showing effect of curatives on durometer hardness before and after aging at 350° F. for 3 days.*

The acrylic rubber recipes in Table VI contain both tetramethyl thiuram monosulfide and sulfur as curatives. These base recipes were an early development; more recently it has been shown that the tetramethyl thiuram monosulfide may be eliminated without adversely affecting the recipe. The sulfur, however, is apparently necessary for heat-resistant stocks. When used in conjunction with the amine, small amounts of sulfur accelerate the cure initially and retard aftercure or hardening upon subsequent exposure to heat. Figure 8 shows the effect of the amine and sulfur on initial cure and subsequent heat resistance at 350° F. In these graphs, the durometer hardness contours are plotted for green and aged vulcanizates from compounded stocks containing different amounts of sulfur and triethyltrimethyl triamine (Trimene Base).

FIG. 9—*Relative curing rates of the polymers studied as determined by scorch tests on Lactoprene EV.*

The data show that (a) increasing amounts of amine curative in the recipe produce harder, more tightly cured vulcanizates, and (b) for a given amount of amine, increasing amounts of sulfur, up to roughly 1 part, appear to accelerate cure, whereas larger amounts have little effect on initial cure. Further examination of the data reveals that small amounts of sulfur have an abnormally large influence in reducing the resulting hardness of the aged vulcanizates. This observation is more evident in the case of low-amine recipes. In fact, by choosing the proper relative amounts of sulfur and amine, say 1 of sulfur and 4 of amine, one obtains a vulcanizate which has the same hardness after aging as initially. These data have proved to be basic information aiding the development of heat-resistant Lactoprene EV compounds.

Scorch tests were made on the polymers in the XP series; a standard recipe was used in which only the amount of triethyltrimethyl triamine was varied. The tests were made in a Mooney viscometer, the MS rotor was used, and the viscometer temperature was maintained at 302° F. (150° C.). Each test was timed from the instant the viscometer cavity was closed.

It will be observed from the data in Figure 9 that when 1 part of curative was used, XP-101-L2 and XP-103-L1 appeared to cure more slowly than either of the other two polymers. When the amount of curative was increased, however, XP-101-L2 cured as rapidly as XP-101-L1. Further, XP-103-L1 exhibited rapid curing up to a point where it failed in the viscometer. Thus, it appeared from the scorch data that the curing characteristics of XP-101-L1, XP-101-L2 and XP-103-L2 were approximately equivalent but XP-103-L1 did not attain an equivalent state of cure. The apparent relatively high curing rates of XP-103-L1 (Recipe B) and XP-103-L2 (Recipe B) are possibly misleading because the high gel content (Table V) could augment cross-linking due to vulcanization.
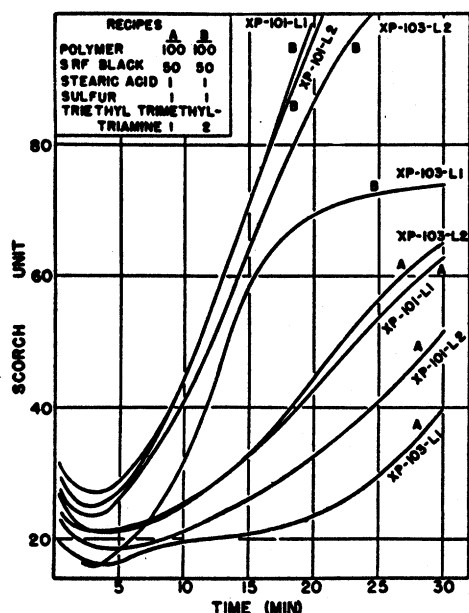
Physical Properties of Vulcanizates

The physical properties of Lactoprene EV vulcanizates have been described elsewhere (1, 2, 7, 8, 11), and it is not within the scope of this paper to consider them in detail. Their outstanding properties include exceptional resistance to heat, oil, light, and oxygen. Such properties as tensile strength, elongation, compression set resistance,

TABLE VIII—TENSILE PROPERTIES OF LACTOPRENE EV VULCANIZATES

Recipe		A	B	C	D	E	F	G	H	I	J
Polymer											
XP-101-L1		100	—	—	—	—	100	—	—	—	—
XP-101-L2		—	100	—	—	—	—	100	—	—	—
XP-103-L1		—	—	100	—	—	—	—	100	—	—
XP-103-L2		—	—	—	100	—	—	—	—	100	—
X-387		—	—	—	—	100	—	—	—	—	100
SRF Black		50	50	50	50	50	—	—	—	—	—
EPC Black		—	—	—	—	—	50	50	50	50	50
Stearic acid		2	2	2	2	—	2	2	2	2	—
Tetramethyl thiuram monosulfide		1	1	1	1	—	1	1	1	1	—
Triethyltrimethyl triamine		2	1	1	2	—	2	2.5	2.5	2	—
Sulfur		2	2	2	2	2	2	2	2	2	2
Zinc oxide		—	—	—	—	5	—	—	—	—	5
Softener (BRT No. 7)		—	—	—	—	5	—	—	—	—	5
Mercaptobenzothiazole		—	—	—	—	1.5	—	—	—	—	1.5
Properties	Cure at 292° F.										
Tensile strength, lb./sq. in.	30 minutes	1670	1420	450	1600	1850	1170	1450	720	700	1980
	60 minutes	1650	1540	660	1690	1920	1420	1810	890	1040	3100
	120 minutes	970	1510	880	1660	1820	1950	1960	1070	1700	3210
	240 minutes	1680	1590	1010	1650	1830	2140	1990	1270	2000	3020
Ultimate elongation, %	30 minutes	300	720	870	370	810	740	540	520	850	500
	60 minutes	290	640	740	330	660	630	530	470	740	540
	120 minutes	170	580	620	300	590	580	380	400	610	440
	240 minutes	250	490	460	240	620	470	430	370	500	370
Modulus at 300% elongation, lb./sq. in.	30 minutes	1670	600	380	1380	510	610	930	730	490	750
	60 minutes	—	790	510	1630	800	780	1190	900	660	1310
	120 minutes	—	850	680	1660	860	1030	1420	1070	960	2030
	240 minutes	—	1060	900	—	830	1390	1590	1260	1310	2230

and hot tear resistance (2, 3, 8, 17), although not outstanding, are acceptable for most specialty applications.

Table VIII gives representative tensile properties of the polymers described here. These results were obtained from work conducted at the Government Laboratories (1), which included data on hot tensile properties and heat resistance not reported here. The curing recipe was one used in earlier work, that is, the sulfur-tetramethyl thiuram monosulfide-triethyltrimethyl triamine recipe, which already has been discussed. The sulfur-triethyltrimethyl triamine recipe is a later one; the amount of triethyltrimethyl triamine used gives maximum heat resistance (Figure 8). In general, the amount of amine used to obtain a given state of cure is a function of the amount and type of black in the recipe. Care should be taken to make comparisons only on the basis of equal states of cure; comparing vulcanizates having equal moduli is adequate provided the amount and type of loading are constant.

Applications

Although vulcanizable polyacrylates are comparatively high in cost, these materials are rapidly claiming a permanent position in the field of specialty elastomers. Increased production may be expected to lead to substantial price reductions. At present, where heat resistance is of paramount importance, the ethyl acrylate copolymer, Lactoprene EV, is superior to the best butadiene-acrylonitrile rubbers by a factor roughly 5. Although nitrile rubbers exhibit better low temperature resistance than does this acrylic rubber, the advantage appears to be potentially with the acrylic rubber because changes in compounding can often compensate for deficient low temperature properties, whereas inferior heat resistance is difficult to circumvent. Although the heat resistance of Lactoprene EV cannot compare with that of silicone rubbers, the advantage is likely to be in favor of the acrylic rubber when high degrees of oil resistance and compression set resistance are also required.

The only acrylic rubbers commercially available (so far as the authors are aware) are the Hycar PA series, two of which, the PA21 and PA31, are basically similar to Lactoprene EV. These rubbers are being introduced in numerous industrial applications in which prolonged resistance to heat is important. Figure 10 shows industrial experimental products containing Lactoprene EV or similar base copolymers.

Summary and Conclusions

Production of Lactoprene EV by the emulsion polymerization method under reflux conditions at atmospheric pressure or slightly higher is fairly simple. A product is obtained that can be used in latex form, or
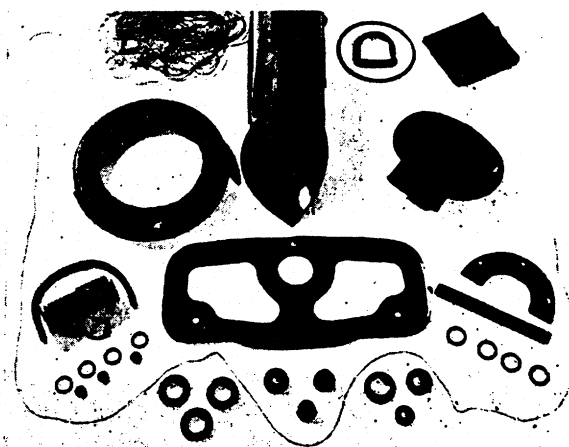

FIG. 10—Molded and extruded acrylic rubber specialty items, including O-rings, flat gaskets, molded sheets, tubing, blown sponge, etc.

with additional processing, in solid raw polymer form. The reflux system affords a convenient method of eliminating most of the heat of reaction from this rapidly polymerizing system. No "shortstoppers" or antioxidants are required. The reaction is rapid and goes to about 95 percent completion. The monomers, being liquids at room temperature, do not require pressure equipment for storage.

The polymer produced is of high molecular weight, versatile in its methods of vulcanization, and has some outstanding properties. The most important of these are its resistance to dry heat, sunlight, oxygen, ozone, and oil; it also has excellent flex life and cut-growth resistance. In addition, white and pastel shade stocks can be compounded and vulcanized.

As the properties of this elastomer become better known and its cost decreases, demands for it will greatly increase.

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